

# **The Equation of State of $\text{UO}_2$** <sup>1</sup>

*I. Iosilevski*<sup>2</sup>, *G. Hyland*<sup>3</sup>, *C. Ronchi*<sup>4</sup>, *E. Yakub*<sup>5</sup>

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<sup>2</sup> Moscow Institute of Physics and Technology (Russia)

<sup>3</sup> University of Warwick, Coventry (United Kingdom)

<sup>4</sup> European Commission, JRC, Institute for Transuranium Elements, Karlsruhe (Germany)  
please, address correspondence here!

<sup>5</sup> Odessa State Medical University (Ukraine)

## ABSTRACT

An international Project supported by INTAS was started in 1994 with the intent of constructing an equation of state for liquid and gaseous  $\text{UO}_2$ , which fully reproduces the consolidated thermodynamic database of this compound. The new equation of state was devised for applications encompassing hypo- and hyper-stoichiometric compositions.

A so-called "Chemical Model" was used for the theoretical description of liquid urania. This model is based on the thermodynamic perturbation theory (TPT) modified in order to account for the specific properties of the system investigated. It describes, in a unified formalism, a *multi-component mixture* of chemically reactive, strongly interacting neutral and charged molecules and atoms.

Comparing the predicted equilibrium vapor pressure with the literature data provided a first validation of the model up to temperatures of the order of 5500 K. A further, positive result is the fairly good agreement of the predicted heat capacity with the experimental values, which extend up to 8000 K. A characteristic feature of non-congruent vaporization in  $\text{UO}_{2\pm x}$  is the production of a very high maximal vapor pressure ( $P_{\max} \sim 1 \text{ GPa}$ ) as well as a substantial oxygen enrichment of the vapor phase over boiling  $\text{UO}_2$  ( $((\text{O/U})_{\max} \sim 7)$ ). The critical point of *truly non-congruent* phase transition in  $\text{UO}_2$  was also calculated. This point *essentially differs* from that defined for a gas-liquid phase transition in *simple liquids*; in particular, we have here  $(\partial P/\partial V)_c \sim (P/V) \neq 0$ . The predicted critical parameters are:  $T_c \approx 10120 \text{ K}$ ,  $P_c \approx 965 \text{ MPa}$ ,  $\rho_c \approx 2.61 \text{ gcm}^{-3}$ .

**KEYWORDS:** *equation of state, heat capacity, high temperatures, non-congruent evaporation, thermodynamic perturbation theory, vapor pressure, uranium dioxide.*

## 1. INTRODUCTION

The equation of state of fluid  $\text{UO}_2$  was first needed in the analysis of hypothetical accidents in Fast Reactors, where temperatures are expected, at which the vapor pressure of the fuel is sufficiently high to produce liquid mass displacements. In the last decade, however, increasing attention was directed on the effects of the atmospheric environment on the vaporization rate of the molten fuel. On the other hand, empirical thermodynamic properties of urania at high temperatures are presently restricted to the near-stoichiometric or congruent-vaporization compositions. The new equation of state was, therefore, devised for applications encompassing hypo- and hyper-stoichiometric compositions.

The main problem in the construction of a physically plausible equation of state of  $\text{UO}_2$  is the complexity of both its liquid and vapor structure: i.e. a presumably highly ionized ionic character of the condensed state, and a weakly ionized molecular character of the gaseous state. Solid  $\text{UO}_2$  is usually described as a pure ionic mixture of  $\text{U}^{+n}$  and  $\text{O}^{-2}$ , and the vapor as a neutral molecular mixture; the structure of the liquid is probably somewhere in between.

## 2. GENERAL APPROACH AND MODEL

A so-called ‘Chemical’ (quasi-molecular) description of *dense liquid*  $\text{UO}_2$  was applied, based on the demonstrated formal correspondence of the partition function of ionic liquids to that of liquids formed of virtual molecular clusters ( Stillinger-Reiss theorem [ <sup>1 2 3</sup> ] ).

In such a model, detailed information is needed to describe the contributions of the internal degrees of freedom of complex (bounded) particles - e.g. energies of ionization and dissociation, excitation energy levels, *etc.* On the other hand, however, the offered advantage is that the renormalized «effective» interaction of free (unbounded) particles is relatively weak, and, furthermore, arbitrary stages of ionization and different structures of complex particles can be composed in the frame of a unified calculation procedure. In principle, once a

proper definition of the effective interaction of free particles is achieved, and the bound states are properly restricted, the model can continually describe the wide variety of states ranging from the presumably highly ionized liquid at very high temperatures, to the ‘cold’ vapor represented by a neutral molecular mixture.

Along with ‘free’  $\text{UO}_2$  a number of ‘clusters’, like  $\text{U}_2\text{O}_4$ ,  $\text{U}_2\text{O}_2$ ,  $\text{U}_2\text{O}_3$ ,  $\text{U}_2\text{O}_5$ , *etc.* as well as free atoms and molecules of uranium and oxygen ( $\text{U}$ ,  $\text{U}_2$ ,  $\text{O}$ ,  $\text{O}_2$ ), and ions ( $\text{UO}_2^+$ ,  $\text{UO}^+$ ,  $\text{U}^+$ ,  $\text{UO}_3^-$ ,  $\text{UO}_2^-$ ,  $\text{O}^-$ ) were included in the picture as distinct species with own partition functions, and parameters of repulsion (intrinsic volumes) and short-range attraction.

This model can be considered as sufficiently realistic for dense vapors and dense, expanded liquids in the high-temperature region of phase coexistence. The liquid phase is essentially described as a set of conventionally distinguishable clusters (mainly with one uranium in the center and several oxygen constituents), which are allowed to freely exchange oxygens and/or electrons.

In a chemical model, the calculation of the equilibrium composition and of the thermodynamic functions starts from the definition of the Helmholtz free energy  $F=F(V,T,N_j)$ , and a set of arbitrary (non-equilibrium) numbers of particles of all species,  $\{N_j\}$ .

The free energy  $F(T,V,\{N_j\})$  is the sum of three contributions: the ideal-gas part,  $\Delta F^{(id)}$ , the interactions of neutral and charged–neutral particles,  $\Delta F_n$ , and of charged–charged particles,  $\Delta F_c$ , i.e.:

$$F(T,V,\{N_j\}) = \Delta F^{(id)} + \Delta F_n + \Delta F_c \quad (1)$$

The set of equilibrium concentrations  $n_i=N_i/V$  ( $n=\sum n_i$ ) corresponds to the conditioned minimum of the free energy, Eq.(1), with respect to the variation of  $N_i$  at constant temperature,  $T$ , and volume,  $V$ , under the constraint of :

1) Conservation of mass  $\sum n_i m_i = \text{Const} \equiv \rho$

2) Chemical proportion:  $(\sum n_i \nu_{ai}) / (\sum n_j \nu_{bj}) = Const$

3) Electro-neutrality:  $\sum n_i Z_i^{(+)} = \sum n_i Z_i^{(-)}$

The general conditions for the free-energy minimum are equivalent to a system of equations for the chemical potentials, or may also be written in the form of mass action law. When explicit expressions for the free energy Eq.(1) are known, the minimization becomes a mere numerical problem.

After the equilibrium composition  $\{n_j\}$  is evaluated, all thermodynamic functions can also be deduced from the thermal and caloric equations of state,  $P=P(T, \{n_i\})$  and  $U=U(T, \{n_i\})$ , which are self-consistently defined as the first derivatives of the free energy. Actually, it is well-known that, in spite of the additional, implicit dependence of  $F(T, V, \{N_j\})$  on  $T$  and  $V$  through the *variable* equilibrium composition, its first *full* derivatives, i.e. pressure, entropy and chemical potentials, are equal to the corresponding *partial* derivatives of the free energy at fixed composition  $\{n_i\}$  at the minimum of  $F(T, V, \{N_j\})$ . However, where the *second* derivatives are concerned (e.g. for heat capacities, compressibility, *etc.*), this additional dependence of the free energy  $F(T, V, \{N_j\})$  must be taken into account *explicitly*. Therefore, these quantities were calculated via a direct numerical differentiation using a program package, developed by V.K.Gryaznov [4].

The contribution of neutral and charged–neutral interactions to the free energy  $\Delta F_n$  was formulated with the thermodynamic perturbation theory (TPT). Application of TPT to a particular system, first necessitates splitting of the microscopic energy of the system into the energy of some ‘unperturbed’, or ‘reference’ system (usually consisting of fully repulsive interactions) and an additional, attractive contribution - in some sense small - representing the ‘perturbation’ energy. The structure and the thermodynamic properties of the ‘unperturbed’ system must be completely defined.

The original approach of Barker and Henderson [5] and Verlet and Weiss [6] was adopted in a modified form, which accounts for the specific properties of the system studied; this model describes, in a unified formalism, a *multi-component mixture* of chemically reactive, strongly interacting neutral and charged molecules and atoms.

The ‘hard-spheres mixture’ approximation [7] was used for the contributions of the ‘reference’ repulsive interactions of all (charged and neutral) species to the free energy. A simplified version of Verlet and Weiss [6] expressions was then assumed for the first-order TPT short-range attractive contributions to  $\Delta F_n$ , within the so-called ‘one-fluid approximation’ for mixtures:

$$\Delta F_n = \Delta F_{HS}^{(0)}(\eta) - \frac{16}{9} \pi \epsilon_{MIX} \sigma_{MIX}^3 \left[ \left( \frac{\sigma_{MIX}}{d(T)} \right)^{12} M_{12}(\eta, T^*) - \left( \frac{\sigma_{MIX}}{d(T)} \right)^6 M_6(\eta, T^*) \right], \quad (2)$$

Here  $M_{12}$  and  $M_6$  are moments of the hard-sphere radial distribution function;  $T^* = kT/\epsilon_{MIX}$  is the reduced temperature and  $\eta = 1/6\pi N V [d(T)]^3$  the packing fraction. Approximate expressions for  $M_{12}$  and  $M_6$  were used as proposed in Ref. [6] for a Lennard-Jones (12-6) potential and conventional combination- and mixing-rules [3].

Using a central-symmetrical Lennard-Jones (12-6) potential for the description of interactions between uranium dioxide molecules (as well as for other components of the liquid mixture) might appear as a too drastic simplification, for most molecules (or ion clusters) do not have a centro-symmetrical structure, and hence a significant anisotropy in the repulsive interactions must be expected [3]. Consequently, the parameters  $\epsilon$  and  $\sigma$  of the Lennard-Jones (12-6) potential should be considered as effective quantities, i.e. as appropriately averaged over all orientations. In this respect, also the definition of the effective molecular diameter  $d(T)$  in Eq.(2) needs a more detailed verification. Therefore, all the used parameters of the Lennard-Jones (12-6) potential,  $\langle \sigma \rangle$ ,  $\langle \epsilon \rangle$  and  $d(T)$ , were analyzed and expressed through “central

components”,  $\sigma_0$ ,  $\varepsilon_0$  and  $d_0(T)$  and a dimensionless anisotropy parameter  $Q$  equal to the ratio of the mean-squared value of the anisotropic contribution to the corresponding isotropic repulsive contribution:

$$d(T) = \frac{d_0(T)}{1 + \frac{\sigma_0}{d_0} \frac{\varepsilon_0 Q^2}{3kT}}; \quad \langle \sigma \rangle = \sigma_0 \left( 1 - \frac{nQ^2}{36} \right); \quad \langle \varepsilon \rangle = \varepsilon_0 \left( \frac{\langle \sigma \rangle}{\sigma_0} \right)^6 \quad (3)$$

Analysis of Eq.(3) shows that, compared to a pre-averaged isotropic potential, the anisotropy of the molecular interaction causes a notable *decrease* of the effective molecular diameter  $\langle \sigma \rangle$ . The effective diameter,  $d(T)$  decreases even more markedly than  $\langle \sigma \rangle$ . Finally, when anisotropy of the repulsive interactions is taken into account, the ratio  $\langle \sigma \rangle/d(T)$  *increases* with respect to the case of central symmetry. Consequently, the effective potential well depth  $\langle \varepsilon \rangle$ , proportional to the sixth power of  $\langle \sigma \rangle/\sigma_0$ , becomes much more pronounced.

We calculated the values of the parameters  $\varepsilon_0$ ,  $\sigma_0$  and  $Q$  from the known bond lengths and atomic radii of the  $\text{UO}_2$  molecule and its heat of vaporization [3]. A value of  $Q \sim 0.66$  was obtained, close to those deduced from experimental data which reproduce density, Gibbs energy and compressibility at the melting point, i.e. the three most sensitive properties of liquid  $\text{UO}_{2.00}$ , when Coulombic contributions are not taken into account.

The non-ideality correction,  $\Delta F_c$ , due Coulomb long-range inter-ionic interactions has a one-parametric form, and consists of a superposition of MSA (Mean Spherical Approximation) + DHSA (Debye-Hückel for Charged Sphere Approximation) [8-9] combined with the “one-fluid” approximation for the case of an ionic mixture with different diameters [10]. In the reported EOS calculations the diameters of all ionic species were assumed to be equal to the diameters of their neutral counterparts.

$$\frac{\Delta F_C}{VKT} \equiv \left( \frac{\Delta F_C}{VKT} \right)_{DHLL} \theta(x, \nu) \equiv \left( \frac{\Delta F_C}{VKT} \right)_{DHLL} \theta(x); \quad x \equiv \langle \sigma \rangle / r_D \quad r_D^2 \equiv \frac{4\pi e^2}{VKT} \sum_{\alpha=1}^2 N_{\alpha} Z_{\alpha}^2 \quad (4)$$

$$\theta(x) = (3\alpha/x^3)[\ln(1+x) - x + x^2] + (1-\alpha)\{[2(1+2x)^{3/2} - 3x^2 - 6x - 2]/x^3\} \quad (5)$$

$$\langle \sigma \rangle \equiv [(\sum_i n_i \sigma_i^3) / (\sum_i n_i)]^{1/3} \quad (6)$$

Here  $(\Delta F_C/VKT)_{DHLL} \equiv -(12\pi r_D^3)^{-1}$  is the reduced Coulomb free energy within Debye–Hückel Limiting Law (DHLL) [10].

It was assumed that charged species of the *same* sign are *not* submitted to the short-range Van der Waals attraction, on account of the strong ordering of the positive and negative charges produced by Coulomb's repulsion. Actually, a significant ionization takes place both in the vapor and in the liquid phase of  $\text{UO}_2$  due to this strong interaction.

### 3. MODEL CALIBRATION

The model was calibrated with a two-stage procedure. The interaction parameters were first evaluated theoretically, and then adjusted to closely reproduce selected properties of molten  $\text{UO}_2$  at the melting point. Properties were chosen, which are sufficiently sensitive to variation of the model parameters, and whose experimental measurements are adequately accurate.

The microscopic parameters for each species were first deduced from independent data sources [3]. A sensitivity study made it possible to select those species whose parameters are dominant ( $\text{UO}_2$ ) or subdominant ( $\text{UO}$ ,  $\text{UO}_3$ ) in defining the properties of liquid  $\text{UO}_2$ . The relative values of all other parameters were then fixed with respect to those of the  $\text{UO}_2$  free molecule. The adjustment of the dominant and subdominant parameters was made on the basis of properties of stoichiometric liquid  $\text{UO}_{2.00}$ : i.e. density, Gibbs free energy, heat capacity, compressibility and oxygen potential at  $T_m=3120$  K. No other properties have been fitted at higher temperatures. Hence the behavior of the equation of state in the broad



temperature range investigated is a property inherent in the physical fundamentals of the model. The calculated values of the thermodynamic functions are presented in Table.1 and compared with other predictions and measurements in Figs. 1 to 3.

#### 4. RESULTS AND DISCUSSION

Comparing the predicted equilibrium vapor pressure with the literature data provided a first validation of the model up to temperatures of the order of 5500 K. A relevant result is the unusual structure of the gas-liquid phase transition boundary, which exhibits a *striking difference* with respect to that of ordinary liquids. This feature is caused by the *non-congruency* of the coexisting phases in  $\text{UO}_{2+x}$ . Both the total vapor pressure and the degree of oxygen enrichment of the vapor phase strongly depend on the evaporation regime. Two distinct pressure-temperature functions  $P=P(T)$  were, therefore, identified and calculated corresponding to the two limiting regimes of: a) *slow* evaporation under "global equilibrium conditions", corresponding to the *boiling* curve, and b) *fast*, non-equilibrium evaporation, called "forced-congruent mode" (FCM), corresponding to *saturation* conditions (SC).

In Fig.1 the curve (1) obtained by enforcing a partially-congruent phase equilibrium - PCE mode, with  $(\text{U/O})_{\text{liq}} = (\text{U/O})_{\text{vap}}$  – is compared with those where non-congruency is governing evaporation (BC and SC curves 2). The predictions of Fisher [13] (curve 3) are also plotted in the same graph. In contrast with non-reacting one-component fluids, uranium dioxide exhibits a coexistence curve and a critical region of an essentially different form. The heat of vaporization is a non-monotonic function of temperature, and the U/O ratio in the vapor phase markedly increases with temperature (Fig 2).

The reliability of the model is corroborated by the fairly good agreement of the predicted heat capacity with the experimental values of Ronchi *et al.*[16], which extend up to 8000 K (Fig.3). In fact, it should be noted, so far, none of the existing liquid  $\text{UO}_2$  models was able to reproduce correctly the observed temperature dependence of  $C_p$ .

A characteristic feature of non-congruent vaporization in  $\text{UO}_{2\pm x}$  is the production of a comparatively high maximal vapor pressure ( $P_{\max} \sim 1$  GPa), as well as a substantial oxygen enrichment,  $(\text{O/U})_{\max} \sim 7$ , of the vapor phase over the boiling liquid, as shown in Fig. 1.

The critical point of the *truly non-congruent* phase transition in  $\text{UO}_2$  was also calculated. This point *essentially differs* from that defined for a gas-liquid phase transition in *simple liquids*; in particular, we have here:  $(\partial P/\partial V)_c \sim (P/V) \neq 0$ .

The predicted critical parameters are:  $T_c \approx 10120$  K,  $P_c \approx 965$  MPa,  $\rho_c \approx 2.61$  g cm<sup>-3</sup> [11].

Details on the results of calculations performed in the high-pressure and high-temperature range  $\{P \leq 10$  GPa,  $T \leq 20000\}$  K will be separately published.

## 5. CONCLUSIONS

The new EOS essentially differs from all previously developed models. The structure of the equation, as well as the broad physical and chemical conditions covered, makes it particularly suitable for applications in nuclear reactor safety analysis. Effective computational algorithms enable numerical calculation of combined phases, as well as chemical and ionization equilibrium in the liquid, described as a strongly interacting uranium-oxygen system. These can be successfully applied to analyze situations involving strongly non-congruent evaporation.

The complete phase diagram of condensed and gaseous  $\text{UO}_{2\pm x}$  up to the *true critical point* has been constructed. For the first time this diagram correctly reproduces the *non-congruent bivariant* nature of the evaporation in the uranium-oxygen system.

The present calculations have the following limitations:

- The excitation partition functions of the complex particles were assumed to be equal to their *ideal-gas* counterparts taken from Glushko's Handbook [12] and from the recommendations of IVTAN-1996 [3], whereby the value of the reduced thermodynamic

potential,  $\Phi^0(T) \equiv G(T)/T$  was used for this extraction. No cut-off procedure and no perturbation of internally bound excited states of complex particles under dense-liquid surrounding were taken into account.

- Only single-stage ionization is included. Therefore, the main charged species in the present model are molecular ions, first of all  $\text{UO}_3^-$ ,  $\text{UO}_2^+$  and  $\text{UO}^+$ . However, performed sensitivity studies show that the presence of other ionic species has little influence on the results.
- Finally, it should be emphasized that first-order TPT does not allow a detailed description of the near critical region, on account of the neglect of fluctuations, which become important in the closest vicinity of the critical point.

Despite these limitations, the present EOS provides the means for a more realistic description of the interplay between thermodynamic aspects and hydrodynamic and diffusive processes occurring during severe reactor accidents.

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Table 1.

Selected properties of the coexisting phases of  $\text{UO}_{2.00}$  along the boiling line

	$T$ (K)	3120	4000	5000	6000	7000	8000
<i>Pressure</i> (MPa)		0.00398	0.147	2.33	20.2	112	388
<i>Density</i> ( $\text{g cm}^{-3}$ )	<u>Liquid</u>	8.8710	8.1257	7.3536	6.5333	5.6797	4.8761
	<u>Vapor</u>	0.00005	0.00105	0.00956	0.0439	0.1535	0.4718
<i>H</i> ( $\text{kJ kg}^{-1}$ )	<u>Liquid</u>	-6406.1	-6005.0	-5628.8	-5238.0	-4779.4	-4158.0
	<u>Vapor</u>	-5394.6	-4962.9	-4339.0	-3454.6	-2519.8	-1935.9
<i>S</i> ( $\text{kJ/kg}^{-1}\text{K}^{-1}$ )	<u>Liquid</u>	1.1620	1.2759	1.3599	1.4305	1.4987	1.5743
	<u>Vapor</u>	1.7776	1.8288	2.1460	2.7825	3.3774	3.2838
<i>C<sub>p</sub></i> ( $\text{kJ/kg}^{-1}\text{K}^{-1}$ )	<u>Liquid</u>	0.5112	0.3992	0.3718	0.4161	0.5242	0.8517
	<u>Vapor</u>	0.8295	1.5394	2.2706	2.5293	2.5331	2.2507
$\beta_T$ ( $10^{-10} \text{ Pa}^{-1}$ )	<u>Liquid</u>	0.395	0.529	0.757	1.17	1.97	3.30
	<u>Vapor</u>	25.95	0.7468	0.0503	0.0059	0.0011	0.0003
$\alpha_T$ ( $10^{-4} \text{ K}^{-1}$ )	<u>Liquid</u>	1.09	0.95	1.08	1.34	1.81	2.83
	<u>Vapor</u>	5.58	7.10	7.01	5.24	4.05	3.50
<i>O/U</i>	<u>Liquid</u>	2.0	2.0	2.0	2.0	2.0	2.0
	<u>Vapor</u>	2.42	2.50	3.07	4.57	6.52	6.36
<i>Ionization</i> (%)	<u>Liquid</u>	9.5	13.0	17.2	21.7	26.3	29.2
	<u>Vapor</u>	3.8	6.7	9.7	5.1	8.6	13.5

## FIGURE CAPTURES

Fig.1. Vapor-liquid phase equilibrium in stoichiometric uranium dioxide.

- 1 - Gas-liquid coexistence in PCE-mode (BC = SC) with pseudocritical point {“PCP” –  $(\partial P/\partial V)_T = 0$ ;  $(\partial^2 P/\partial V^2)_T = 0$ ;  $(\partial^3 P/\partial V^3)_T = 0$ }.
- 2 - Boiling (BC) and saturation (SC) curves in total equilibrium (EOS “INTAS-99”) [14]
- 3 - Total vapor pressure calculated by Fischer [13] with pseudocritical point (PCP).

Fig.2. U/O ratio of coexisting phases on the boiling and saturation curves.

- 1 - Open circles - calculations of Green & Leibovitz [14]
  - 2 - Open diamonds - O/U ratio from the calculated composition of Ohse *et al.* [15]
  - 3 - Squares -O/U ratio (total) reconstructed from calculations of Fischer [13]
  - 4 - Solid line - present work
- BC - boiling curve  
SC - saturation curve  
CP – true critical point  
PCP – pseudo-critical point in Fischer’s calculations  
CCT - point of maximal temperature on SC (*cricondenterm*)

Fig.3. Heat capacity of liquid uranium dioxide.

Comparison of predictions and measurements [16].

- 1 - Measurements of Ronchi *et al.* [16]
- 2 - Cp calculated by Fischer [13]
- 3 - Present calculation.

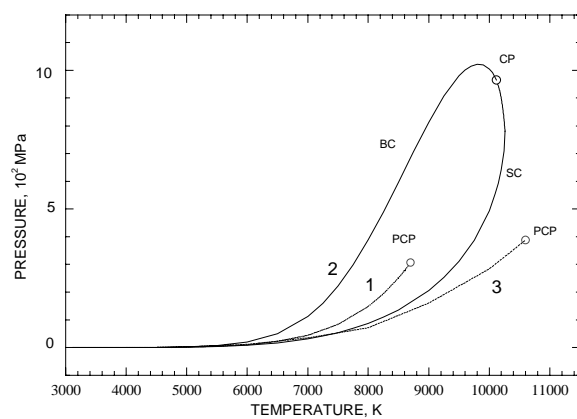


FIG. 1

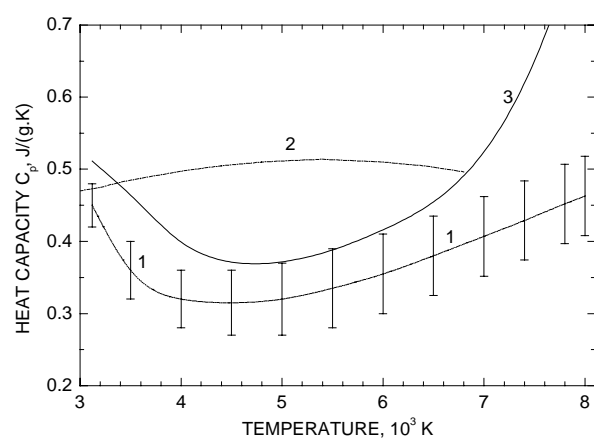


FIG. 3

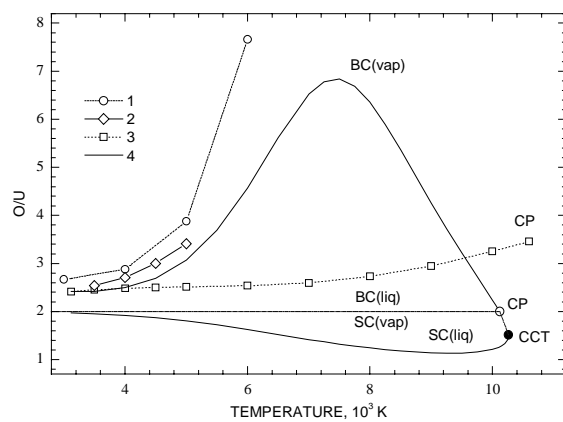


FIG. 2